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(21) International Application Number: PCT/US99/11549 (22) International Filing Date: 26 May 1999 (26.05.99) (30) Priority Data: 60/087,152 29 May 1998 (29.05.98) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors: BENNETT, Alison, Margaret, Anne; 507 Falkirk Road, Wilmington, DE 19803 (US). FELDMAN, Jerald; 16 Cinnamon Drive, Hockessin, DE 19707 (US). MCCORD, Elizabeth, Forrester; 514 Hemlock Drive, Hockessin, DE 19707 (US). (74) Agent: EVANS, Craig, H.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AE, AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, UZ, VN, YU, ZA, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: COPOLYMERIZATION OF OLEFINS (57) Abstract <p>Ethylene and/or propylene, and α-olefins may be copolymerized by contacting them with certain iron or cobalt complexes of selected 2,6-pyridinecarboxaldehydebis(imines) and 2,6-diacylpyridinebis(imines). The polymers produced, some of which are novel, are useful as molding resins.</p>		

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TITLE

COPOLYMERIZATION OF OLEFINS

FIELD OF THE INVENTION

5 Selected iron and cobalt complexes of
2,6-pyridinecarboxaldehydebis(imines) and
2,6-diacylpyridinebis(imines) are catalysts for the
copolymerization of ethylene and/or propylene and
 α -olefins. Novel polymers may be produced.

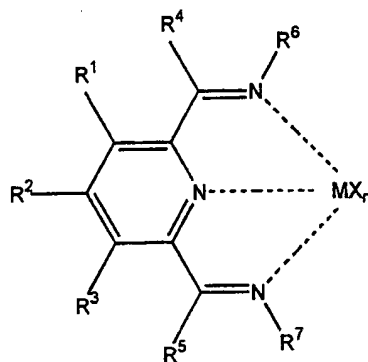
10 FIELD OF THE INVENTION

Copolymers of ethylene and/or propylene and
 α -olefins, such as linear low density polyethylene
(LLDPE) are important items of commerce, millions of
tons being produced annually. These polymers are used
15 in a myriad of ways, such as for fiber, films, molding
resins, etc. In most cases, ethylene and α -olefins are
copolymerized using a catalyst, often a transition
metal compound or complex. These catalysts may vary in
cost per unit weight of polymer produced, the structure
20 of the polymer produced, the possible need to remove
the catalyst from the polymer, the toxicity of the
catalyst, etc. Due to the commercial importance of
copolymerizing ethylene, new polymerization catalysts
are constantly being sought.

25 B. L. Small, et al., J. Am. Chem. Soc., vol. 120,
p. 4049-4050 (1998), and G. J. P. Britovsek, et al.,
J. Chem. Soc., Chem. Commun., p. 849-850 (1998) report
the polymerization of ethylene using catalysts
containing Fe or Co complexes of
30 2,6-pyridinecarboxaldehydebis(imines) and
2,6-diacylpyridinebis(imines). Copolymerization of
 α -olefins and ethylene are not reported.

SUMMARY OF THE INVENTION

This invention concerns a first polymerization
35 process, comprising, contacting, at a temperature of
about -100°C to about $+200^{\circ}\text{C}$, a compound of the formula



(II)

with one or both of ethylene and propylene, and an olefin of the formula $H_2C=CHR^{21}$ and:

- 5 (a) a first compound W, which is a neutral Lewis acid capable of abstracting X^- an alkyl group or a hydride group from M to form WX^- , $(WR^{20})^-$ or WH^- and which is also capable of transferring an alkyl group or a hydride to M, provided that WX^- is a weakly
10 coordinating anion; or

- (b) a combination of second compound which is capable of transferring an alkyl or hydride group to M and a third compound which is a neutral Lewis acid which is capable of abstracting X^- , a hydride or an
15 alkyl group from M to form a weakly coordinating anion;

wherein:

M is Co or Fe;

each X is an anion;

- 20 n is 1, 2 or 3 so that the total number of negative charges on said anion or anions is equal to the oxidation state of a Fe or Co atom present in (II);

R^1 , R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

- 25 R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl;

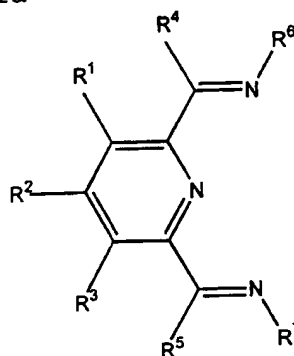
R^6 and R^7 are aryl or substituted aryl;

R^{20} is alkyl; and

- 30 R^{21} is alkyl.

This invention also concerns a second polymerization process, comprising contacting, at a

temperature of about -100°C to about $+200^{\circ}\text{C}$, a Co[II], Co[III], Fe[II] or Fe[III] complex of a tridentate ligand of the formula



(I)

5

with one or both of ethylene and propylene, and an olefin of the formula $\text{H}_2\text{C}=\text{CHR}^{21}$ wherein:

R^1 , R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

10

R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl; and

R^6 and R^7 are aryl or substituted aryl;

15

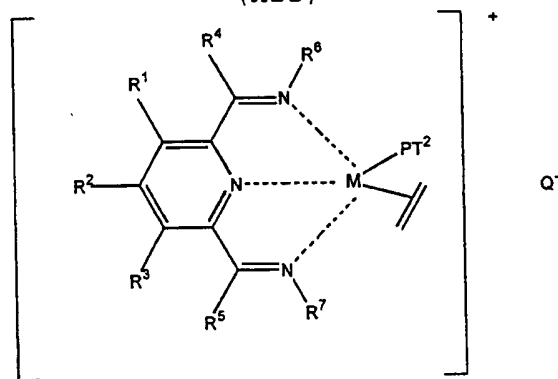
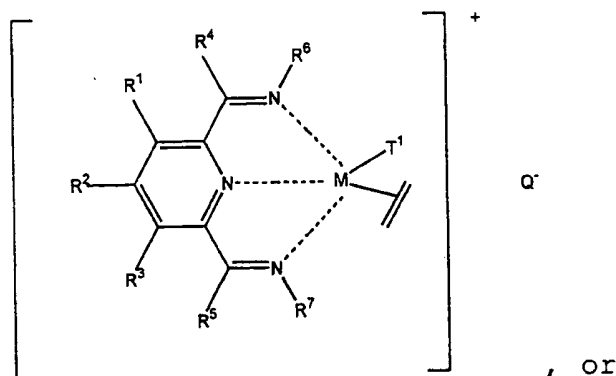
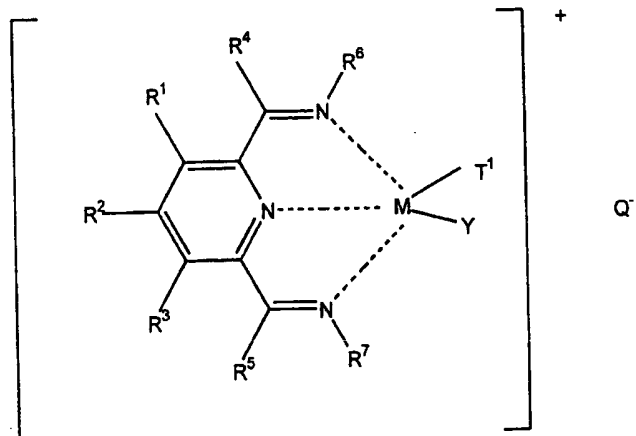
R^{21} is alkyl;

20

and provided that a Co[II], Co[III], Fe[II] or Fe[III] atom also has bonded to it an empty coordination site or a ligand that may be displaced by said ethylene, and a ligand that may add to said ethylene.

25

This invention also concerns a third polymerization process, comprising, contacting, at a temperature of about -100°C to about $+200^{\circ}\text{C}$, one or both of ethylene and propylene, an olefin of the formula $\text{H}_2\text{C}=\text{CHR}^{21}$, and a compound of the formula



wherein:

M is Co or Fe;

10 R^1 , R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl; and

15 R^6 and R^7 are aryl or substituted aryl;

R^{21} is alkyl;

T^1 is hydride or alkyl or any other anionic ligand into which ethylene or an α -olefin can insert;

Y is a neutral ligand capable of being
5 displaced by ethylene or a vacant coordination site;

Q is a relatively non-coordinating anion;

P is a divalent polyolefin group; and

T^2 is an end group.

DETAILS OF THE INVENTION

10 Herein, certain terms are used. Some of them are:

o A "hydrocarbyl group" is a univalent group containing only carbon and hydrogen. If not otherwise stated, it is preferred that hydrocarbyl groups herein contain 1 to about 30 carbon atoms.

15 o By "substituted hydrocarbyl" herein is meant a hydrocarbyl group which contains one or more substituent groups which are inert under the process conditions to which the compound containing these groups is subjected. The substituent groups also do
20 not substantially interfere with the process. If not otherwise stated, it is preferred that substituted hydrocarbyl groups herein contain 1 to about 30 carbon atoms. Included in the meaning of "substituted" are heteroaromatic rings. All of the hydrogen atoms may be
25 substituted for, as in trifluoromethyl.

o By "(inert) functional group" herein is meant a group other than hydrocarbyl or substituted hydrocarbyl which is inert under the process conditions to which the compound containing the group is
30 subjected. The functional groups also do not substantially interfere with any process described herein that the compound in which they are present may take part in. Examples of functional groups include halo (fluoro, chloro, bromo and iodo), ether such as
35 $-OR^{18}$ wherein R^{18} is hydrocarbyl or substituted hydrocarbyl. In cases in which the functional group may be near a cobalt or iron atom, such as R^4 and R^5 , the functional group should not coordinate to the metal

atom more strongly than the groups in compounds containing R^4 and R^5 , which are shown as coordinating to the metal atom, that is they should not displace the desired coordinating group.

5 o By an "alkyl aluminum compound" is meant a compound in which at least one alkyl group is bound to an aluminum atom. Other groups such as alkoxide, hydride, and halogen may also be bound to aluminum atoms in the compound.

10 o By "neutral Lewis base" is meant a compound, which is not an ion, which can act as a Lewis base. Examples of such compounds include ethers, amines, sulfides, and organic nitriles.

 o By "cationic Lewis acid" is meant a cation
15 which can act as a Lewis acid. Examples of such cations are sodium and silver cations.

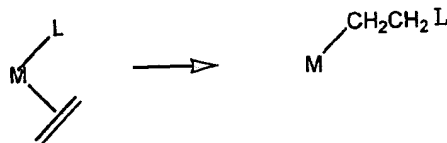
 o By relatively noncoordinating (or weakly coordinating) anions are meant those anions as are generally referred to in the art in this manner, and
20 the coordinating ability of such anions is known and has been discussed in the literature, see for instance W. Beck., et al., Chem. Rev., vol. 88 p. 1405-1421 (1988), and S. H. Stares, Chem. Rev., vol. 93, p. 927-942 (1993), both of which are hereby included by
25 reference. Among such anions are those formed from the aluminum compounds in the immediately preceding paragraph and X^- , including $R^9_3AlX^-$, $R^9_2AlClX^-$, $R^9AlCl_2X^-$, and " R^9AlOX^- ", wherein R^9 is alkyl. Other useful noncoordinating anions include BAF^- {BAF =
30 tetrakis[3,5-bis(trifluoromethyl)phenyl]borate}, SbF_6^- , PF_6^- , and BF_4^- , trifluoromethanesulfonate, p-toluenesulfonate, $(R_fSO_2)_2N^-$, and $(C_6F_5)_4B^-$.

 o By an empty coordination site is meant a
potential coordination site that does not have a ligand
35 bound to it. Thus if an ethylene molecule is in the proximity of the empty coordination site, the ethylene or other olefin molecule may coordinate to the metal atom.

o By a "divalent polyolefin group" is meant a group -Z- which contains one or more ethylene and/or α -olefin repeat units.

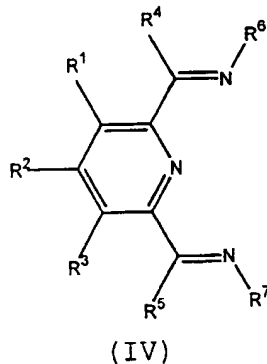
o By a ligand that may add to ethylene, propylene, or an α -olefin is meant a ligand coordinated to a metal atom into which an ethylene molecule (or a coordinated ethylene molecule) may insert to start or continue a polymerization. For instance, this may take the form of the reaction (wherein L is a ligand):

10



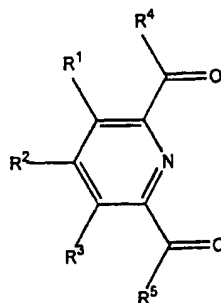
Note the similarity of the structure on the left-hand side of this equation to compound (IX) (see below).

Compounds useful as ligands herein in iron and cobalt complexes are diimines of 2,6-pyridinedicarboxaldehyde or 2,6-diacetylpyridines of the general formula



wherein R^1 , R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group, R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl, and R^6 and R^7 are aryl or substituted aryl.

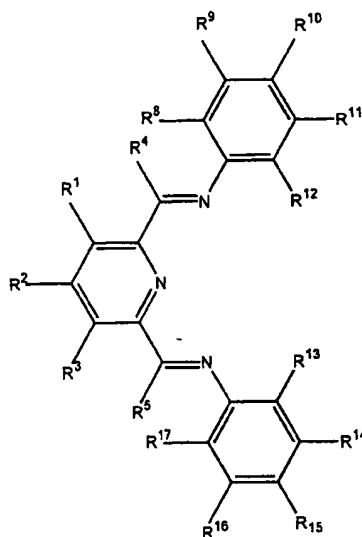
(IV) may be made by the reaction of a compound of the formula



(VI)

with a compound of the formula H₂NR⁶ or H₂NR⁷, wherein
 R¹, R² and R³ are each independently hydrogen,
 5 hydrocarbyl, substituted hydrocarbyl, or an inert
 functional group, R⁴ and R⁵ are each independently
 hydrogen, hydrocarbyl or substituted hydrocarbyl, R⁴
 and R⁵ are each hydrocarbyl or substituted hydrocarbyl,
 and R⁶ and R⁷ are aryl or substituted aryl. These
 10 reactions are often catalyzed by carboxylic acids, such
 as formic acid.

Preferred compounds of formula (IV) and compounds
 in which (IV) is a ligand are those of compound (III)
 [note



(III)

15 that (III) is a subset of (IV)], whether present in
 compounds such as (I), (II), (IV), (VII), (IX) and
 (XII). In (III), and hence in (I), (II), (IV) (VII),
 20 (IX) and (XII) that match the formula of (III), it is
 preferred that:

R¹, R² and R³ are hydrogen; and/or

R^1 and R^3 are hydrogen and R^2 is trifluoromethyl; and/or

R^9 , R^{10} , R^{11} , R^{14} , R^{15} and R^{16} is each independently halogen, alkyl containing 1 to 6 carbon atoms, or hydrogen, and it is more preferred that each of these is hydrogen; and/or

R^{10} and R^{15} are methyl; and/or

R^8 and R^{13} is each independently halogen, phenyl or alkyl containing 1 to 6 carbon atoms, and it is especially preferred that each R^8 and R^{13} is alkyl containing 1-6 carbon atoms and is more preferred that R^8 and R^{13} are methyl; and/or

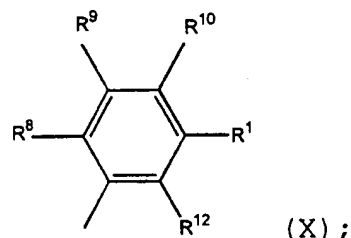
R^{12} and R^{17} is each independently halogen, phenyl, hydrogen, or alkyl containing 1 to 6 carbon atoms, and it is especially preferred that each R^{12} and R^{17} is alkyl containing 1-6 carbon atoms, and it is more preferred that R^{12} and R^{17} are methyl; and/or

R^4 and R^5 are each independently halogen, thioalkyl, hydrogen or alkyl containing 1 to 6 carbon atoms, and it is especially preferred that R^4 and R^5 are each independently hydrogen or methyl; and/or

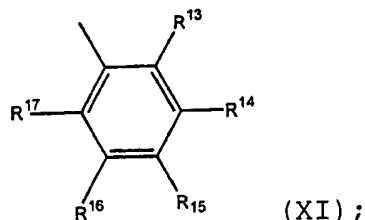
R^8 , R^{10} , R^{13} , R^{15} and R^{17} are hydrogen, and R^9 , R^{11} , R^{14} and R^{16} are hydrocarbyl or substituted hydrocarbyl.

Also in (III), and hence in (I), (II), (IV) (VII), (IX) and (XII) that match the formula of (III), it is preferred that:

R^6 is



R^7 is



R^8 and R^{13} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

5 R^9 , R^{10} , R^{11} , R^{14} , R^{15} and R^{16} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R^{12} and R^{17} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert
10 functional group;

and provided that any two of R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} and R^{17} that are vicinal to one another, taken together may form a ring.

Specific preferred compounds (III) [and also in
15 (I), (II), (IV), (VII), (IX) and (XII)] are:

R^1 , R^2 , R^3 , R^9 , R^{11} , R^{14} and R^{16} are hydrogen, and R^4 , R^5 , R^8 , R^{10} , R^{12} , R^{13} , R^{15} and R^{17} are methyl;

R^1 , R^2 , R^3 , R^9 , R^{10} , R^{11} , R^{14} , R^{15} and R^{16} are hydrogen, R^8 and R^{13} are chloro, and R^4 , R^5 , R^{12} and R^{17}
20 are methyl;

R^1 , R^2 , R^3 , R^9 , R^{10} , R^{11} , R^{12} , R^{14} , R^{15} , R^{16} and R^{17} are hydrogen, R^4 and R^5 are methyl, and R^8 and R^{13} are phenyl;

R^1 , R^2 , R^3 , R^4 , R^5 , R^9 , R^{10} , R^{11} , R^{14} , R^{15} , and R^{16}
25 are hydrogen, and R^8 , R^{12} , R^{13} and R^{17} are i-propyl; and

R^1 , R^2 , R^3 , R^4 , R^5 , R^{10} , R^8 , R^{10} , R^{13} , R^{15} and R^{17} are hydrogen, and R^9 , R^{11} , R^{14} and R^{16} are trifluoromethyl.

In the polymerization processes described herein,
30 it can be seen from the results that it is preferred that there be at least some steric crowding caused by the tridentate ligand about the Co or Fe atom. Therefore, it is preferred that groups close to the metal atom be relatively large. It is relatively

simple to control steric crowding if (III) is the tridentate ligand, since control of steric crowding can be achieved simply by controlling the size of R^8 , R^{12} , R^{13} and R^{16} . These groups may also be part of fused
5 ring systems, such as 9-anthracenyl.

In the first polymerization process it is preferred that X is chloride, bromide and tetrafluoroborate. It is also preferred that M is Fe[II] or Fe[III].

10 In the first polymerization process described herein an iron or cobalt complex (II) is contacted with ethylene, an α -olefin and a neutral Lewis acid W capable of abstracting X^- , hydride or alkyl from (II) to form a weakly coordinating anion, and must alkylate
15 or be capable of adding a hydride ion to the metal atom, or an additional alkylating agent or an agent capable of adding a hydride anion to the metal atom must be present. The neutral Lewis acid is originally uncharged (i.e., not ionic). Suitable neutral Lewis
20 acids include SbF_5 , Ar_3B (wherein Ar is aryl), and BF_3 . Suitable cationic Lewis acids or Bronsted acids include NaBAF, silver trifluoromethanesulfonate, HBF_4 , or $[C_6H_5N(CH_3)_2]^+ [B(C_6F_5)_4]^-$. In those instances in which
25 (II) (and similar catalysts which require the presence of a neutral Lewis acid or a cationic Lewis or Bronsted acid), does not contain an alkyl or hydride group already bonded to the metal atom, the neutral Lewis acid or a cationic Lewis or Bronsted acid also
alkylates or adds a hydride to the metal or a separate
30 alkylating or hydriding agent is present, i.e., causes an alkyl group or hydride to become bonded to the metal atom.

It is preferred that R^{20} contains 1 to 4 carbon atoms, and more preferred that R^{20} is methyl or ethyl.

35 For instance, alkyl aluminum compounds (see next paragraph) may alkylate (II). However, not all alkyl aluminum compounds may be strong enough Lewis acids to abstract X^- or an alkyl group from the metal atom. In

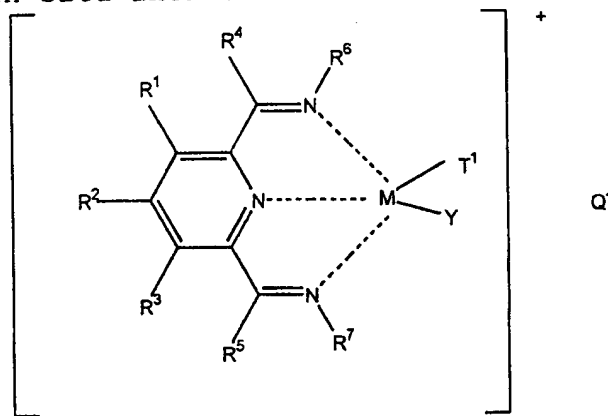
that case a separate Lewis acid strong enough to do the abstraction must be present.

A preferred neutral Lewis acid, which can alkylate the metal, is a selected alkyl aluminum compound, such as R^{19}_3Al , R^{19}_2AlCl , R^{19}_2AlCl , and " $R^{19}AlO$ " (alkylaluminoxanes), wherein R^{19} is alkyl containing 1 to 25 carbon atoms, preferably 1 to 4 carbon atoms. Suitable alkyl aluminum compounds include methylaluminoxane (which is an oligomer with the general formula $[MeAlO]_n$), $(C_2H_5)_2AlCl$, $C_2H_5AlCl_2$, and $[(CH_3)_2CHCH_2]_3Al$.

Metal hydrides such as $NaBH_4$ may be used to bond hydride groups to the metal M.

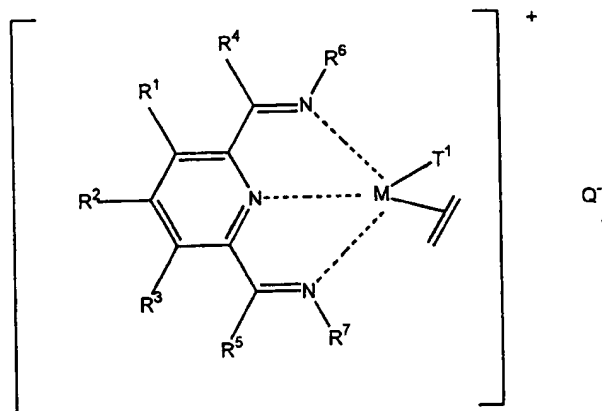
In the second polymerization process described herein a cobalt or iron complex of (I) is either added to the polymerization process or formed in situ in the process. In fact, more than one such complex may be formed during the course of the process, for instance formation of an initial complex and then reaction of that complex to form a living ended polymer containing such a complex.

Examples of such complexes which may be formed initially in situ include



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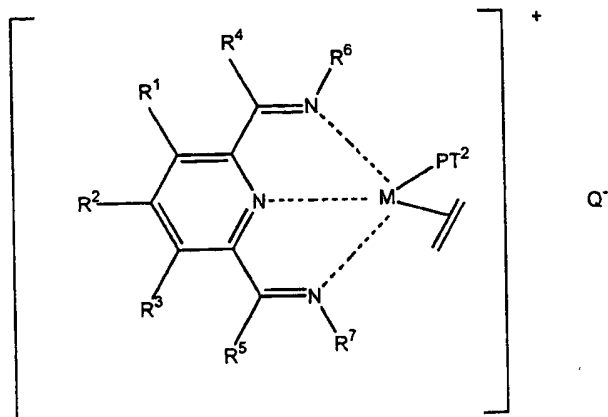
and



(XII)

wherein R^1 through R^7 , and M are as defined above, T^1 is hydride or alkyl or any other anionic ligand into which ethylene or an α -olefin can insert, Y is a neutral ligand capable of being displaced by ethylene, propylene or an α -olefin, or a vacant coordination site, the "parallel lines" are an ethylene molecule coordinated to the metal, and Q is a relatively non-coordinating anion. Complexes may be added directly to the process or formed in situ. For instance, (VII) may be formed by the reaction of (II) with a neutral Lewis acid such as an alkyl aluminum compound. Another method of forming such a complex in situ is adding a suitable iron or cobalt compound such as iron [II] acetylacetonate, (I) and an alkyl aluminum compound. Other metal salts in which anions similar to acetylacetonate are present, and which may be removed by reaction with the Lewis or Bronsted acid. For instance metal halides and carboxylates (such as acetates) may be used, particularly if they are slightly soluble in the process medium. It is preferred that these precursor metal salts be at least somewhat soluble in the process medium.

After the polymerization has started, the complex may be in a form such as



(IX)

wherein R¹ through R⁷, M, and Q are as defined above,
 and P is a divalent polymeric groups containing repeat
 5 units derived from ethylene and/or propylene and/or an
 α -olefin, and T² is an end group, for example the
 groups listed for T¹ above. Those skilled in the art
 will note that (IX) is in essence a polymer containing
 a so-called living end. It is preferred that M be in
 10 +2 oxidation state in (VII), (VIII) and (IX).
 Compounds such as (VII), (IX) and (XII) may or may not
 be stable away from an environment similar to that of
 the polymerization process, but they may be detected by
 NMR spectroscopy, particularly one or both of ¹H and ¹³C
 15 NMR, and particularly at lower temperatures. Such
 techniques, especially for polymerization
 "intermediates" of these types are known, see for
 instance World Patent Application 96/23010, especially
 Examples 197-203, which is hereby included by
 20 reference.

(VII), (IX) and (XII) may also be used, in the
 absence of any "co-catalysts" or "activators" to
 polymerize ethylene in a third polymerization process.
 Except for the ingredients in the process, the process
 25 conditions for the third process, such as temperature,
 pressure, polymerization medium, etc., may be the same
 as for the first and second polymerization processes,
 and preferred conditions for those processes are also
 preferred for the third polymerization process.

In all the polymerization processes herein, the temperature at which the ethylene copolymerization is carried out is about -100°C to about $+200^{\circ}\text{C}$, preferably about -60°C to about 150°C , more preferably about -50°C to about 100°C .

For copolymerization one or more α -olefins of the formula $\text{H}_2\text{C}=\text{CHR}^{21}$ may be used. It is preferred that R^{21} have 1 to 18 carbon atoms, more preferably 2 to 8 carbon atoms, and/or that R^{21} be n-alkyl. Since ethylene is polymerized considerably faster than propylene and most α -olefins by these catalysts, in order to obtain substantial incorporation of the α -olefin(s), the concentration of ethylene in the polymerization should preferably be relatively low compared to the concentration of the propylene and α -olefin(s). This will most often entail using ethylene at a low partial pressure, preferably less than 1.0 MPa, more preferably less than 500 kPa, and especially preferably less than 300 kPa (all these ethylene partial pressures are absolute partial pressures). If the α -olefin is a gas its partial pressure should preferably be relatively high. If the α -olefin is used in the liquid phase, its liquid concentration should preferably be relatively high.

NMR analysis of the product copolymers shows that the end groups are both saturated and unsaturated (olefinic), although saturated end groups usually outnumber unsaturated end groups. It is suspected that saturated end groups may arise through initiation and chain transfer involving alkyl aluminum compounds present in the polymerization. Unsaturated end groups are believed to arise through a β -hydride elimination-type mechanism. A small proportion of the olefinic ends appear to be internal olefins, but the majority of the olefinic ends are usually α -olefins (terminal olefins).

It is preferred that the product copolymer have at least 0.5 mole percent (total), more preferably 0.75

mole percent (total), especially preferably 1 mole percent (total), and highly preferably at least about 2 mole percent (total) of α -olefin(s) incorporated into the product copolymer. When 1-hexene is a comonomer the percent incorporated versus short chain branches, assuming all such branches are butyl, is shown in the following Table.

Mole Percent 1-Hexene	n-Butyl Branches per 1000 C Atoms
0.5	2.5
0.75	3.7
1.0	4.9
2.0	9.6
10.0	41.7

In copolymers of ethylene and $\text{H}_2\text{C}=\text{CHR}^{21}$ produced herein the polymer will contain $-\text{R}^{21}$ branches and methyl branches. The total amount of $\text{H}_2\text{C}=\text{CHR}^{21}$ is taken as the total of the $-\text{R}^{21}$ branches in the polymer, calculated according to a suitable formula, for example branches per 1000 carbon atoms or mole percent of $\text{H}_2\text{C}=\text{CHR}^{21}$ incorporated. It is believed that the methyl branches in the copolymer are associated with the end groups (but are not the end groups themselves). for example, end groups associated with methyl branches are

~~~~~ $\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$  and  
~~~~~ $\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

are the methyl branch associated groups for 1-pentene and 1-hexene respectively (and similar structures for higher and lower homologs), wherein "~~~~" is the remainder of the polymer chain. Such groups are detectable by ^{13}C -NMR because methyl branches near the chain ends are somewhat different than methyl branches further in the interior of the polymer chain, see for instance the Examples herein. Note that the group beyond the methine carbon atom (towards the chain end) is actually $-\text{R}^{21}$. In other words the methyl branch is attached to the same carbon atom as an $-\text{R}^{21}$ group. Not

all polymer chains have such chain ends, but usually at least some of them are present in these copolymers.

A preferred monomer combination is ethylene and one or more olefins of the formula $H_2C=CHR^{21}$.

5 During the polymerization process often some or most of the olefin comonomer $H_2C=CHR^{21}$ will be unused in the polymerization. Testing of this unused comonomer at the end of the polymerization process shows that it is usually essentially unaltered (not isomerized), so
10 it may be recovered and recycled into the polymerization, if desired. This recycling may take place without purification, or the comonomer may be purified being recycled to the polymerization, as by distillation.

15 The polymerization processes herein may be run in the presence of various liquids, particularly aprotic organic liquids. The catalyst system, ethylene, propylene, α -olefin, and polyolefin may be soluble or insoluble in these liquids, but obviously these liquids
20 should not prevent the polymerization from occurring. Suitable liquids include alkanes, cycloalkanes, selected halogenated hydrocarbons, and aromatic hydrocarbons. Specific useful solvents include hexane, toluene and benzene.

25 The copolymerizations herein may also initially be carried out in the solid state [assuming (II), (III) (IV) or (VII) is a solid] by, for instance, supporting (II), (III) (IV) or (VII) on a substrate such as silica or alumina or an organic substrate such as a polymer,
30 activating it with the Lewis (such as W, for instance an alkylaluminum compound) or Bronsted acid and exposing it to an olefin. The support may also be able to take the place of the Lewis or Bronsted acid, for instance an acidic clay such as montmorillonite.

35 Another method of making a supported catalyst is to start a polymerization or at least make an iron or cobalt complex of another olefin or oligomer of an olefin such as 1-hexene on a support such as silica or

alumina. These "heterogeneous" catalysts may be used to catalyze polymerization in the gas phase or the liquid phase. By gas phase is meant that the monomers are transported to contact with the catalyst particle while they are in the gas phase.

Hydrogen may be used as a chain transfer agent in all of the polymerization processes described herein.

In all of the polymerization processes described herein oligomers and copolymers of ethylene and/or propylene are made. They may range in molecular weight from oligomers, to lower molecular weight oils and waxes, to higher molecular weight polyolefins. One preferred product is a polymer with a degree of polymerization (DP) of about 10 or more, preferably about 40 or more. By "DP" is meant the average number of repeat (monomer) units in a polymer molecule.

In the Examples, the pressures given are gauge pressures. Methods of NMR analysis for polymer branching, and the notation used herein to describe the branching as determined by ^{13}C NMR, are found in U.S. Patent 5,880,241 (equivalent of World Patent Application 96/23010), which is hereby included by reference. Syntheses of the diimine ligands and their Co and Fe complexes are found in B. L. Small, et al., J. Am. Chem. Soc., vol. 120, p. 4049-4050 (1998), and G. J. P. Britovsek, et al., J. Chem. Soc., Chem. Commun., p. 849-850 (1998), which are both hereby included by reference. The following abbreviations and terms are used:

DSC - differential scanning calorimetry

GC - gas chromatography

GPC - gel permeation chromatography

HOF - heat of fusion

IBAO-0.65 - isobutylaluminum produced by the reaction of triisobutylaluminum with 0.65 equivalents of water

MMAO-3A - methylaluminoxane containing some isobutyl groups

Mn - number average molecular weight

MeOH - methanol

5 PMAO - polymethylaluminoxane

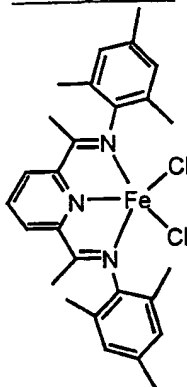
PMAO-IP - polymethylaluminoxane (Akzo, 12.8 weight percent aluminum in toluene)

PDI - weight average molecular weight divided by number average molecular weight (Mn)

10 TCB - 1,2,4-trichlorobenzene

Tm - melting point

Example 1



(XIII)

15 In a drybox under a nitrogen atmosphere, (XIII) (8 mg, 0.015 mmol) was weighed into a Schlenk flask and slurried in 20 ml anhydrous toluene. 1-Octene (3 ml, dried by distillation from sodium) was added and the Schlenk flask sealed and removed from the drybox. The flask was flushed well with ethylene and pressurized to 35 kPa. PMAO-IP (0.8 ml) was added and the solution turned orange and warmed. After 30 min the reaction was quenched by addition of MeOH. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 2.7 g white polymer. DSC (10°C/min, N₂); Tm = 123.2°C, shoulder on peak at 100°C. GPC (120°C, TCB); Mn = 1500, PDI = 5.6. The lowered (from pure polyethylene) melting point shows incorporation of comonomer.

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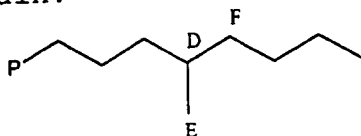
Example 2

In a drybox under a nitrogen atmosphere, (XIII)
(7.5 mg, 0.014 mmol) was weighed into a Schlenk flask
and slurried in 10 ml anhydrous toluene. 1-Hexene (3
5 ml, dried by distillation from sodium) was added and
the Schlenk flask sealed and removed from the drybox.
The flask was flushed well with ethylene and
pressurized to 35 kPa. PMAO-IP (0.8 ml) was added and
the solution turned green and warmed. After 30 min the
10 reaction was quenched by addition of MeOH. The solid
polymer was filtered, washed well with MeOH/10% HCl,
MeOH and finally acetone and dried under vacuum. Yield
= 6.0 g white polymer. DSC (10°C/min, N₂); T_m =
126.3°C, shoulder on low temperature side of peak. GPC
15 (120°C, TCB); Mn = 2420, PDI = 8.0. ¹³C-NMR analysis
indicated a total of 2.5 mol% 1-hexene incorporation.
The branching was >75% butyl branches (1,2 or 2,1
incorporation). Amyl and methyl branches were also
observed at low levels. No ethyl or propyl branches
20 were observed.

Example 3

In a drybox under a nitrogen atmosphere, (XIII)
(2.0 mg) was weighed into a flask and slurried in 35 ml
1-hexene (Aldrich, 99+%, filtered through Al₂O₃ and
25 stored over activated molecular sieves). The flask was
stoppered and removed from the drybox. PMAO-IP (1.0
ml) was added to 5 ml anhydrous toluene and placed in a
vial and removed from the drybox. The 1-hexene slurry
was placed in a 100 ml Parr® stirred autoclave under an
30 atmosphere of nitrogen. Stirring was started and the
reactor heated to 50°C. The PMAO solution was then
added to the reactor with 140 kPa ethylene. After 10
min the reaction was quenched by addition of MeOH. The
solid polymer was filtered, washed well with MeOH/10%
35 HCl, MeOH and finally acetone and dried under vacuum.
Yield = 7.8 g white polymer. DSC (10°C /min., N₂); T_m
= 102.0°C with a minor peak at 112.0°C. GPC (120°C,
trichlorobenzene); Mn = 2534, PDI = 2.3. ¹³C-NMR

analysis (5 weight percent in TCB, 120°C) indicated a total of 3.9 mol% 1-hexene incorporation. Of this most resulted in butyl branches (1,2 or 2,1 incorporation). Trace amounts of amyl and methyl branches were also observed. No ethyl or propyl branches were observed. The observed NMR is given below together with the assignments. The assignments of D, E and F are shown in the structure below, with "P" representing the rest of the polymer chain.



10

| Frequency | PPM | Height | Assignment |
|-----------|--------|--------|-------------------------|
| 3816.348 | 37.946 | 32.9 | MB ₄ |
| 3716.490 | 36.954 | 2.0 | |
| 3498.618 | 34.787 | 4.3 | |
| 3455.364 | 34.357 | 67.6 | αγ ⁺ B |
| 3415.848 | 33.964 | 36.4 | 4B ₄ |
| 3320.796 | 33.019 | 2.7 | D |
| 3224.143 | 32.058 | 10.8 | 3B ₆₊ , 3EOC |
| 3052.729 | 30.354 | 75.6 | γγ ⁺ B |
| 3004.669 | 29.876 | 1417.0 | γγ ⁺ B |
| 2953.405 | 29.366 | 50.9 | 3B ₄ |
| 2728.058 | 27.125 | 67.0 | βγ ⁺ B |
| 2340.374 | 23.271 | 37.6 | 2B ₄ |
| 2290.178 | 22.772 | 10.1 | 2B ₅₊ , 2EOC |
| 1994.877 | 19.835 | 2.3 | E |
| 1412.818 | 14.048 | 40.1 | 1B ₄₊ , 1EOC |

Example 4

In a drybox under a nitrogen atmosphere, (XIII)
 (6.1 mg, 0.011 mmol) was weighed into a Schlenk flask
 and slurried in 10 ml anhydrous toluene. 1-Hexene (5
 ml, dried by distillation from sodium) and anhydrous
 toluene (15 ml) were added and the Schlenk flask sealed
 and removed from the drybox. The flask was cooled to
 0°C and then flushed well with ethylene and pressurized
 to 35 kPa. PMAO-IP (0.9 ml) was added and the solution
 turned green and warmed. After 30 min the reaction was
 quenched by addition of MeOH. The solid polymer was
 filtered, washed well with MeOH/10% HCl, MeOH and

finally acetone and dried under vacuum. Yield = 2.7 g white polymer. DSC (10°C/min, N₂); T_m = 127.6°C, shoulder on low temperature side of peak. GPC (120°C, trichlorobenzene); M_n = 2120, PDI = 19.1. ¹³C-NMR analysis indicated a total of 1.2 mol% 1-hexene incorporation. Only methyl and butyl branches were observed (1,2 or 2,1 incorporation).

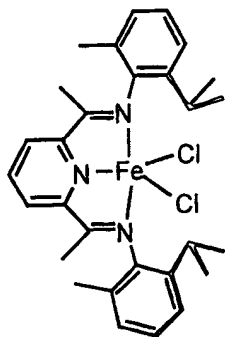
Comparative Example A

In a drybox under a nitrogen atmosphere, (XIII) (7.5 mg, 0.014 mmol) was weighed into a Schlenk flask and slurried in 10 ml anhydrous toluene. Anhydrous toluene (30 ml) was added and the Schlenk sealed and removed from the drybox. The flask was cooled to 0°C and then flushed well with ethylene and pressurized to 35 kPa. PMAO-IP (0.9 ml) was added and the solution turned orange and warmed. After 30 min the reaction was quenched by addition of MeOH. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 1.9 g white polymer. DSC (10°C/min, N₂); T_m = 132.7°C. GPC (120°C, trichlorobenzene); M_n = 2900, PDI = 19.1.

Example 5

In a drybox under nitrogen, (XIII) (1.8mg) was placed in 1-hexene (25 ml, Aldrich 99+%, filtered through activated Al₂O₃ and stored over activated molecular sieves) in a Hoke cylinder and sealed. PMAO-IP (0.9 ml) was placed in 2 ml anhydrous toluene in a vial and sealed. The containers were removed from the drybox. The 1-hexene slurry was placed in a Parr® stirred autoclave. Ethylene (70 kPa) was added, stirring started and the mixture heated to 75°C. The PMAO-IP solution was added to the reactor with an additional 160 kPa ethylene. After 81 min the reaction was quenched by addition of MeOH. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 1.61 g white polymer. DSC (10°C/min., N₂); T_m(2nd heat) = 115.5°C. GPC (135°C, TCB); M_n = 1090, PDI = 1.8.

^{13}C -NMR analysis indicated a total of 1.4 mol% 1-hexene incorporation. The observed number of short chain branches per 1000 CH_2 groups were methyl 1.9, butyl 7.1 and amyl 1.4.



(XIV)

5

Example 6

In a drybox under nitrogen, (XIV) (6.0 mg) was placed in a Schlenk flask and anhydrous toluene (5 ml) and 1-hexene (10 ml, Aldrich 99+%, filtered through activated Al_2O_3 and stored over activated molecular sieves) added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and PMAO-IP (0.9 ml) added. After 30 min the reaction was quenched by addition of MeOH/10% HCl. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 2.43g white polymer. DSC ($10^\circ\text{C}/\text{min.}$, N_2); $T_m(2^{\text{nd}} \text{ heat}) = 123.1^\circ\text{C}$, 109.2°C (broad). GPC (135°C , TCB); $M_n = 1620$, PDI = 8.4. ^{13}C -NMR analysis indicated a total of 2.1 mol% 1-hexene incorporation. The observed number of short chain branches per 1000 CH_2 groups were methyl 0.8, butyl 10.5 and amyl 1.5.

20

Example 7

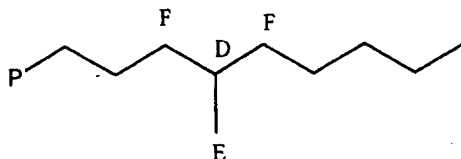
In a drybox under nitrogen, (XIII) (3.0 mg) was placed in a Schlenk flask and anhydrous toluene (5 ml) and 1-hexene (10 ml, Aldrich 99+%, filtered through activated Al_2O_3 and stored over activated molecular sieves) added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and MMAO-3A (0.45ml, Akzo, 6.42 wt% Al in heptane) added. After 30 min the reaction was quenched by addition of

30

MeOH/10% HCl. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 1.1 g white polymer. DSC (10°C/min., N₂); T_m(2nd heat) = 121.0°C, ~80°C (broad).
5 GPC (135°C, TCB); Mn = 1507, PDI = 6.6. ¹³C-NMR analysis indicated a total of 6.4 mol% 1-hexene incorporation. The observed number of short chain branches per 1000 CH₂ groups was methyl 1.9 butyl 30.5 and amyl 0.5. In addition, isobutyl ends are observed
10 on the polymer (from the MMAO activator), and in this instance the isobutyl ends are not included in the methyl branch total.

Example 8

In a drybox under nitrogen, (XIII) (6.3 mg) was
15 placed in a Schlenk flask and anhydrous toluene (5 ml) and 1-heptene (10 ml, distilled from Na) added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and PMAO-IP (0.9 ml) added. After 30 min the reaction was quenched by
20 addition of MeOH/10% HCl. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 0.87g white polymer. DSC (10°C/min., N₂); T_m(2nd heat) = 122.3°C. GPC (135°C, TCB); Mn = 2680, PDI = 5.9.
25 ¹³C-NMR analysis (10 weight percent in TCB, 120°C) indicated a total of 5.3 mol% 1-heptene incorporation. The observed number of short chain branches per 1000 CH₂ groups were methyl 2.3, and amyl 24.6. The observed NMR is given below together with the
30 assignments. The assignments of D, E and F are shown in the structure below, with "P" representing the rest of the polymer chain.



| Frequency | PPM | Height | Assignment |
|-----------|--------|--------|--------------------------|
| 3857.777 | 38.358 | 8.4 | |
| 3820.931 | 37.992 | 58.6 | MB ₄₊ |
| 3750.443 | 37.291 | 7.4 | F |
| 3622.817 | 36.022 | 3.5 | |
| 3502.133 | 34.822 | 10.8 | |
| 3455.675 | 34.360 | 132.6 | α B ₃₊ |
| 3398.004 | 33.787 | 4.6 | |
| 3323.778 | 33.049 | 4.9 | D |
| 3274.116 | 32.555 | 81.1 | 3B ₅ |
| 3223.386 | 32.051 | 18.3 | 3B ₆₊ , 3EOC |
| 3142.218 | 31.243 | 7.9 | |
| 3080.808 | 30.633 | 30.3 | |
| 3051.438 | 30.341 | 108.0 | γ^+ B |
| 3003.378 | 29.863 | 2327.2 | γ^+ γ B |
| 2961.192 | 29.444 | 43.1 | |
| 2776.429 | 27.606 | 8.3 | |
| 2727.835 | 27.123 | 106.6 | $\beta\gamma^+$ B |
| 2688.319 | 26.730 | 74.4 | 4B ₅ |
| 2449.621 | 24.357 | 4.8 | |
| 2289.422 | 22.764 | 98.3 | 2B ₅₊ , 2EOC |
| 1994.654 | 19.833 | 4.8 | E |
| 1408.323 | 14.003 | 95.4 | 1B ₄₊ , 1EOC |

Comparative Example B

In a drybox under nitrogen, (XIII) (6.3 mg) was placed in a Schlenk flask and anhydrous toluene (15 ml) added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and PMAO-IP (0.9 ml) added. After 30 min the reaction was quenched by addition of MeOH/10% HCl. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 1.1 g white polymer. DSC (10°C/min., N₂); T_m(2nd heat) = 127.2°C. GPC (135°C, TCB); M_n = 1220, PDI = 9.0. No branching was observed in the ¹³C-NMR analysis.

Example 9

In a drybox under nitrogen, (XIV) (6.0 mg) was placed in a Schlenk flask and anhydrous toluene (5 ml) and 1-heptene (10 ml, distilled from Na) added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and PMAO-IP (0.9 ml) added. After 30 min the reaction was quenched by addition of MeOH/10% HCl. The solid polymer was

filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 0.95 g white polymer. DSC (10°C/min., N₂); T_m(2nd heat) = 123.4°C, 110.6°C. GPC (135°C, trichlorobenzene); M_n = 2540, PDI = 5.3. ¹³C-NMR analysis indicated a total of 3.0 mol% 1-heptene incorporation. The observed number of short chain branches per 1000 CH₂ groups were methyl 0.7, and amyl 14.4.

Comparative Example C

10 In a drybox under nitrogen, (XIV) (6.0 mg) was placed in a Schlenk flask and anhydrous toluene (15 ml) added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and PMAO-IP (0.9 ml) added. After 30 min the reaction was
15 quenched by addition of MeOH/10% HCl. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. DSC (10°C/min., N₂); T_m(2nd heat) = 131.2°C. GPC (135°C, TCB); M_n = 1410, PDI = 20.0. No branching was observed
20 in the ¹³C-NMR analysis.

Example 10

In a drybox under nitrogen, (XIII) (6.1 mg) was placed in a Schlenk flask and anhydrous toluene (5 ml) and 1-pentene (10 ml, filtered through activated Al₂O₃
25 and stored over activated molecular sieves) added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and PMAO-IP (0.9 ml) added. After 30 min the reaction was quenched by addition of MeOH/10% HCl. The solid polymer was
30 filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 0.82 g white polymer. DSC (10°C/min., N₂); T_m(2nd heat) = 117.8°C, ~90°C (broad). GPC (135°C, TCB); M_n = 1028, PDI = 3.8. ¹³C-NMR analysis indicated a total of 10.0
35 mol% 1-pentene incorporation. The observed number of short chain branches per 1000 CH₂ groups were methyl 6.3, and propyl 50.9. GC analysis of the supernatant

indicated negligible isomerization of the unreacted 1-pentene.

Example 11

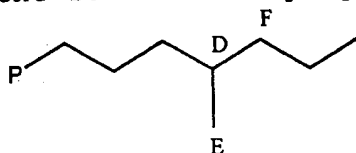
In a drybox under nitrogen, (XIII) (1.4 mg) was placed in ~6 ml anhydrous toluene in a vial. 1-Pentene (30 ml, filtered through activated Al_2O_3 and stored over activated molecular sieves), anhydrous toluene (5 ml) and PMAO (0.5ml, Akzo, 10.9 wt% Al in toluene) was placed in a Hoke cylinder and sealed. The containers were removed from the drybox. The 1-pentene slurry was placed in a 100ml Parr® stirred autoclave. Ethylene (41 kPa) was added and stirring started. The catalyst solution was added to the reactor with an additional 10psi ethylene. After 12 min the reaction was quenched by addition of MeOH. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 1.6 g white polymer. DSC (10°C/min., N_2); $T_m(2^{\text{nd}}$ heat) = 123.6°C. ^{13}C -NMR analysis indicated a total of 0.8 mol% 1-pentene incorporation.

Example 12

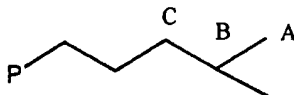
In a drybox under nitrogen, (XIII) (3.0 mg) was placed in a Schlenk flask and anhydrous toluene (5 ml) and 1-pentene (10 ml, filtered through activated Al_2O_3 and stored over activated molecular sieves) added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and MMAO-3A (0.45 ml, Akzo, 6.42 wt% Al in heptane) added. After 30 min the reaction was quenched by addition of MeOH/10% HCl. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 1.9 g white polymer. DSC (10°C/min., N_2); $T_m(2^{\text{nd}}$ heat) = 128.0°C. GPC (135°C, TCB); M_n = 1716, PDI = 7.0. ^{13}C -NMR analysis (10 weight percent in TCB, 120°C) indicated a total of 4.5 mol% 1-pentene incorporation. The observed number of short chain branches per 1000 CH_2 groups were methyl 2.4, propyl 21.7, and amyl 0.4. Any isopropyl or isobutyl end

groups present due to initiator are not counted in the methyl group total. The observed NMR is given below together with the assignments. The assignments of A, B, C, D, E and F are shown in the structure below, with

5 "P" representing the rest of the polymer chain.



and



| Frequency | PPM | Height | Assignment |
|-----------|--------|--------|-------------------------|
| 3990.433 | 39.677 | 6.8 | F |
| 3950.917 | 39.284 | 7.1 | C |
| 3829.166 | 38.074 | 5.9 | |
| 3792.320 | 37.708 | 53.3 | MB ₃₊ |
| 3752.270 | 37.309 | 8.0 | |
| 3696.200 | 36.752 | 58.8 | 3B ₃ |
| 3497.018 | 34.771 | 9.4 | |
| 3451.628 | 34.320 | 105.7 | $\alpha\gamma^+B$ |
| 3398.228 | 33.789 | 5.0 | |
| 3293.031 | 32.743 | 7.2 | 2B ₅ , D |
| 3222.543 | 32.042 | 21.0 | 3B ₆₊ , 3EOC |
| 3139.773 | 31.219 | 6.5 | |
| 3050.061 | 30.327 | 120.9 | $\gamma\gamma^+B$ |
| 3002.535 | 29.855 | 2288.8 | $\gamma^+\gamma^+B$ |
| 2960.883 | 29.440 | 56.7 | |
| 2823.646 | 28.076 | 8.6 | B |
| 2763.838 | 27.481 | 12.4 | |
| 2724.856 | 27.094 | 104.6 | $\beta\gamma^+B$ |
| 2442.904 | 24.290 | 2.4 | |
| 2288.578 | 22.756 | 22.5 | 2B ₅₊ , 2EOC |
| 2276.297 | 22.634 | 17.2 | A |
| 2029.055 | 20.175 | 63.0 | 2B ₃ |
| 1987.937 | 19.766 | 8.0 | E |
| 1459.812 | 14.515 | 60.5 | 1B ₃ |
| 1407.480 | 13.995 | 21.1 | 1B ₄₊ , 1EOC |

10

Example 13

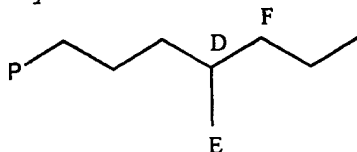
In a drybox under nitrogen, (XIII) (3.0 mg) was placed in a Schlenk flask and anhydrous toluene (5 ml) and 1-pentene (10 ml, filtered through activated Al₂O₃ and stored over activated molecular sieves) added. The

15

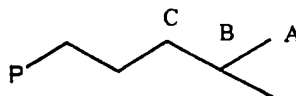
flask was sealed and removed from the drybox. The flask was flushed with ethylene and AlEt_3 (0.3 ml, 0.1M solution in toluene/hexane) and $\text{B}(\text{C}_6\text{F}_5)_3$ (0.0146 g in 0.5 ml toluene) were added. After 30 min the reaction was quenched by addition of MeOH/10% HCl. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 0.21 g white polymer. DSC ($10^\circ\text{C}/\text{min.}$, N_2); $T_m(2^{\text{nd}}$ heat) = 127.6°C . ^{13}C -NMR analysis indicated a total of 0.64 mol% 1-pentene incorporation.

Example 14

In a drybox under nitrogen, (XIII) (3.0 mg) was placed in a Schlenk flask and anhydrous toluene (5 ml) and 1-pentene (10 ml, filtered through activated Al_2O_3 and stored over activated molecular sieves) added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and IBAO-0.65 (0.45ml, Akzo, 3.5 wt% Al in toluene) added. After 90 min the reaction was quenched by addition of MeOH/10% HCl. The solid polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. DSC ($10^\circ\text{C}/\text{min.}$, N_2); $T_m(2^{\text{nd}}$ heat) = 115.5°C (bimodal). GPC (135°C , TCB); $M_n = 1957$, PDI = 8.9. ^{13}C -NMR analysis (10 weight percent in TCB, 140°C) indicated a total of 8.2 mol% 1-pentene incorporation. The observed number of short chain branches per 1000 CH_2 groups were methyl 3.4, and propyl 39.0. (amyl not integrated due to overlap). Any isopropyl or isobutyl end groups present due to initiator are not counted in the methyl group total. The assignments of A, B, C, D, E and F are shown in the structure below, with "P" representing the rest of the polymer chain.



and



| Frequency | PPM | Height | Assignment |
|-----------|--------|--------|-------------------------|
| 3991.407 | 39.687 | 10.5 | F |
| 3951.357 | 39.289 | 8.9 | C |
| 3840.285 | 38.184 | 15.2 | |
| 3802.371 | 37.807 | 179.7 | MB ₃₊ |
| 3753.243 | 37.319 | 16.2 | |
| 3706.251 | 36.852 | 200.4 | 3B ₃ |
| 3577.023 | 35.567 | 5.4 | |
| 3509.740 | 34.898 | 27.2 | |
| 3462.214 | 34.425 | 345.1 | $\alpha\gamma^+B$ |
| 3391.192 | 33.719 | 7.8 | |
| 3295.606 | 32.769 | 9.8 | D |
| 3271.576 | 32.530 | 8.2 | 3B ₅ |
| 3218.710 | 32.004 | 21.9 | 3B ₆₊ , 3EOC |
| 3159.970 | 31.420 | 15.7 | |
| 3084.142 | 30.666 | 35.7 | |
| 3047.296 | 30.300 | 320.8 | $\gamma\gamma^+B$ |
| 2998.168 | 29.811 | 3551.0 | $\gamma^+\gamma^+B$ |
| 2954.915 | 29.381 | 64.8 | |
| 2822.483 | 28.064 | 10.4 | B |
| 2777.093 | 27.613 | 16.5 | |
| 2727.965 | 27.125 | 337.0 | $\alpha\gamma^+B$ |
| 2565.629 | 25.510 | 3.9 | |
| 2455.091 | 24.411 | 13.7 | |
| 2282.076 | 22.691 | 24.5 | 2B ₅₊ , 2EOC |
| 2270.862 | 22.579 | 23.9 | A |
| 2029.494 | 20.180 | 216.3 | 2B ₃ |
| 1986.774 | 19.755 | 13.3 | E |
| 1451.173 | 14.429 | 206.8 | 1B ₃ |
| 1397.239 | 13.893 | 24.1 | 1B ₄₊ , 1EOC |
| 1355.054 | 13.473 | 6.7 | |

Note: Existence of Me branches implies that these do not arise from the activator.

5

Example 15

In a drybox under nitrogen, (XIII) (4.5 mg) was placed in a Schlenk flask and anhydrous toluene (5 ml) and 4-methyl-1-pentene (10 ml, filtered through activated Al₂O₃ and stored over activated molecular
 10 sieves) added. The flask was sealed and removed from the drybox. The flask was flushed with ethylene and PMAO-IP (0.9 ml) added. After 30 min the reaction was quenched by addition of MeOH/10% HCl. The solid
 15 polymer was filtered, washed well with MeOH/10% HCl, MeOH and finally acetone and dried under vacuum. Yield = 4.65 g white polymer. DSC (10°C/min., N₂); T_m(2nd

heat) = 121.4°C, 100.6°C (broad). GPC (135°C, TCB); Mn = 1740, PDI = 5.0. ¹³C-NMR analysis indicated a total of 4.1 mol% 4-methyl-1-pentene incorporation.

Example 16

5 In a dry box under nitrogen atmosphere, the iron complex 2,6-diacetylpyridinebis(2,4,6-trimethylphenylimine)iron dichloride (1.5 mg, 2.86 μmol) was weighed into a vial and diluted to 10 ml with toluene (Aldrich, Anhydrous 99.8%). An aliquot of 3 ml
10 containing 0.45 mg (0.86 μmol) of catalyst was transferred to the injector vessel with 50 ml of toluene. To a second vessel, 100 ml of CaH₂ purified 1-octene (Aldrich, 98%) was mixed with 2 ml of MMAO-3A (Akzo Nobel). These solutions were transferred by
15 pressure to a 600 ml Parr® autoclave reactor. The polymerization temperature was 120°C and the ethylene pressure was 860 kPa, adjusted by a pressure regulator. The polymerization was run for 30 min. The reaction was quenched with methanol. The solid polymer was
20 filtered and washed with acetone. Yield = 2.68 g, DSC (10°C/min): T_m = 126.2°C, HOF = 212 J/g.

Example 17

In a dry box under nitrogen atmosphere, an aliquot of 3 ml from the same stock solution of Example 16 was
25 diluted with 50 ml of toluene and transferred to the injector vessel. To the second vessel, 80 ml of CaH₂ purified 1-octene (Aldrich, 98%) was mixed with 2 ml of MMAO-3A (Akzo Nobel). These solutions were transferred by pressure to a 600 Parr® autoclave reactor. The
30 polymerization temperature was 60°C and the ethylene pressure was 860 kPa, adjusted by a pressure regulator. The polymerization was run for 30 min. The reaction was quenched with methanol. The solid polymer was filtered, washed with acetone, and dried under vacuum.
35 Yield = 38.9 g, DSC (10°C/min): T_m = 132.7 °C, HOF = 226 J/g.

Example 18

In a dry box under nitrogen atmosphere, the iron complex [2,6-diacetylpyridinebis{(3,5-trifluoromethyl)phenylimine}] iron dichloride was weighed (6 mg, 9.7 μmol) and diluted to 100 ml of toluene (Aldrich, anhydrous, 99.8%) and spiked with 20 drops of methylene chloride (Aldrich). To this solution, 5.6 ml of MMAO-3A (Akzo Nobel) was added. This catalyst solution was transferred via cannula to a feed vessel of a catalyst pump. The pumping rate was constant for 15 min, resulting in 3.8 mg of catalyst used. For the comonomer, 85 ml of CaH_2 purified 1-hexene (Aldrich, 99%) was transferred to the reactor through a feed vessel. A 500 ml Zipperclave® reactor was charged with 165 ml of hexane (Aldrich, anhydrous, 95%+). The polymerization was run at 50°C and 1.01 MPa of ethylene pressure. After 30 min, the reaction was quenched with methanol. The solid polymer was filtered, washed with acetone and dried under vacuum. Yield = 1.4 g, DSC (10°C/min): $T_m = 126.6^\circ\text{C}$, with a shoulder at about 118°C. HOF = 194 J/g. GPC $M_w = 11345$, PDI = 7.44.

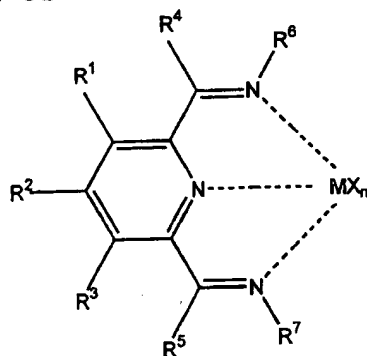
Comparative Example

Example 18 above was repeated with the same iron complex solution available in the catalyst pump feed vessel. No comonomer was added to this example. The catalyst pumping rate was constant for the first 15 min of the run, resulting in 2.3 mg of catalyst used. A 500 ml Zipperclave® reactor was charged with 250 ml of hexane (Aldrich, anhydrous, 95%). The polymerization was run at 50°C and 1.01 MPa of ethylene pressure. After 30 min, the reaction was quenched with methanol. The solid polymer was filtered, washed with acetone and dried under vacuum. Yield = 3.4 g, DSC (10°C/min): $T_m = 130.3^\circ\text{C}$, HOF = 278 J/g. $M_w = 14434$, PDI = 6.03

CLAIMS

What is claimed is:

1. A polymerization process, comprising,
contacting, at a temperature of about -100°C to about
5 $+200^{\circ}\text{C}$, a compound of the formula



(II)

with one or both of ethylene and propylene, an α -olefin of the formula $\text{H}_2\text{C}=\text{CHR}^{21}$, and:

- 10 (a) a first compound W, which is a neutral Lewis acid capable of abstracting X^- and alkyl group or a hydride group from M to form WX^- , WR^{20} or WH and which is also capable of transferring an alkyl group or a hydride to M, provided that WX^- is a weakly
15 coordinating anion; or

- (b) a combination of a second compound which is capable of transferring an alkyl or hydride group to M and a third compound which is a neutral Lewis acid which is capable of abstracting X^- , a hydride or an
20 alkyl group from M to form a weakly coordinating anion;

wherein:

M is Co or Fe;

each X is an anion;

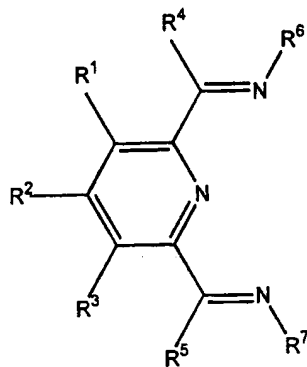
- 25 n is 1, 2 or 3 so that the total number of negative charges on said anion or anions is equal to the oxidation state of a Fe or Co atom present in (II);

R^1 , R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

- 30 R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group, or substituted hydrocarbyl;

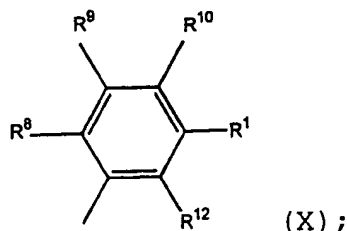
R^6 and R^7 are aryl or substituted aryl;
 R^{20} is alkyl; and
 R^{21} is alkyl

2. A polymerization process, comprising
 5 contacting, at a temperature of about -100°C to about $+200^{\circ}\text{C}$, a Co[II], Co[III], Fe[II] or Fe[III] complex of a tridentate ligand of the formula

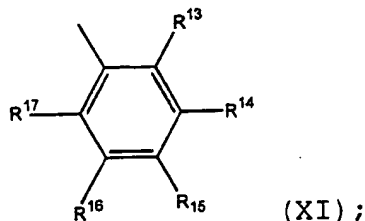


(I)

- 10 with one or both of ethylene and propylene, and an α -olefin of the formula $\text{H}_2\text{C}=\text{CHR}^{21}$, wherein:
 R^1 , R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;
 15 R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl;
 R^6 and R^7 are aryl or substituted aryl; and
 R^{21} is alkyl;
 20 and provided that a Co[II], Co[III], Fe[II] or Fe[III] atom also has bonded to it an empty coordination site or a ligand that may be displaced by said ethylene, and a ligand that may add to said ethylene.
 25 3. The process as recited in claim 1 or 2 wherein ethylene is present and propylene is not present.
 4. The process as recited in claim 2 wherein:
 R^6 is



R^7 is



R^8 and R^{13} are each independently hydrogen,
 5 hydrocarbyl, substituted hydrocarbyl or an inert
 functional group;

R^9 , R^{10} , R^{11} , R^{14} , R^{15} and R^{16} are each
 independently hydrogen, hydrocarbyl, substituted
 hydrocarbyl or an inert functional group;

10 R^{12} and R^{17} are each independently hydrogen,
 hydrocarbyl, substituted hydrocarbyl or an inert
 functional group;

and provided that any two of R^8 , R^9 , R^{10} , R^{11} , R^{12} ,
 R^{13} , R^{14} , R^{15} , R^{16} and R^{17} that are vicinal to one
 15 another, taken together may form a ring.

5. The process as recited in claim 4 wherein:

R^1 , R^2 and R^3 are hydrogen;

R^9 , R^{10} , R^{11} , R^{14} , R^{15} and R^{16} is each
 independently halogen, alkyl containing 1 to 6 carbon
 20 atoms, or hydrogen;

R^8 and R^{13} is each independently halogen, phenyl
 or alkyl containing 1 to 6 carbon atoms;

R^{12} and R^{17} is each independently halogen,
 phenyl, hydrogen, or alkyl containing 1 to 6 carbon
 25 atoms; and

R^4 and R^5 are each independently hydrogen or
 alkyl containing 1 to 6 carbon atoms.

6. The process as recited in claim 5 wherein R^4
 and R^5 are each hydrogen or methyl.

7. The process as recited in claim 5 wherein X is chloride, bromide or tetrafluoroborate.

8. The process as recited in claim 5 wherein said neutral Lewis acid is an alkyl aluminum compound.

5 9. The process as recited in claim 8 wherein said alkyl aluminum compound is polymethylaluminumoxane.

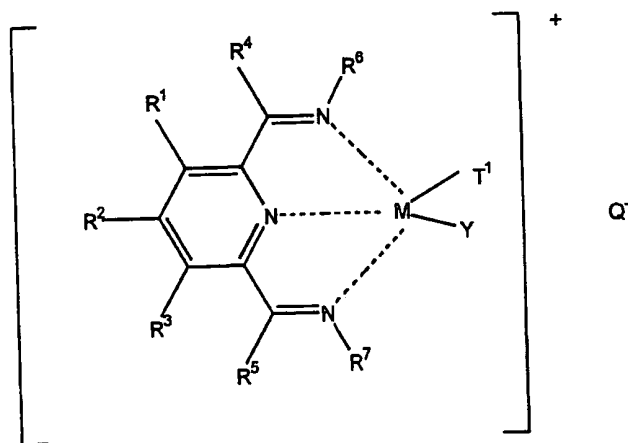
10. The process as recited in claim 5 wherein said temperature is about -50°C to about 100°C .

10 11. The process as recited in claim 1 wherein M is Fe.

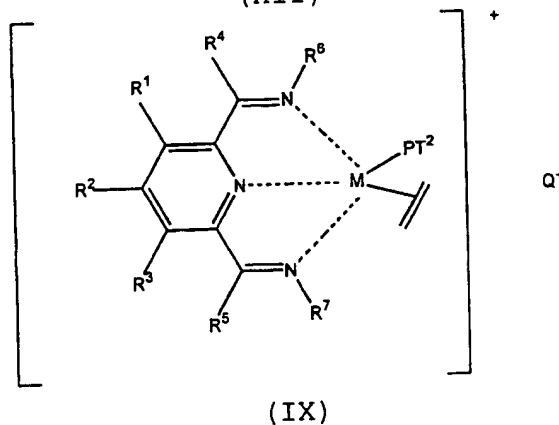
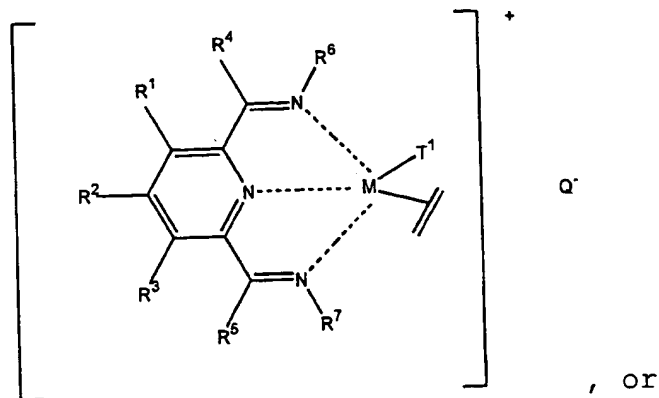
12. The process as recited in claim 2 wherein said complex is an Fe[II] or Fe[III] complex.

13. The process as recited in claim 1, 2, 11 or 12 wherein R^{21} is n-alkyl.

15 14. A polymerization process, comprising, contacting, at a temperature of about -100°C to about $+200^{\circ}\text{C}$, one or both of ethylene and propylene, an α -olefin of the formula $\text{H}_2\text{C}=\text{CHR}^{21}$, and a compound of the formula



(VII)



5 wherein:

 M is Co or Fe;

 R¹, R² and R³ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

10 R⁴ and R⁵ are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl;

 R⁶ and R⁷ are aryl or substituted aryl;

 R²¹ is alkyl;

15 T¹ is hydride or alkyl or any other anionic ligand into which ethylene or an α -olefin can insert;

 Y is a neutral ligand capable of being displaced by ethylene or a vacant coordination site;

 Q is a relatively non-coordinating anion;

20 P is a divalent polyolefin group; and

 T² is an end group.

15. The process as recited in claim 14 wherein ethylene is present and propylene is not present.

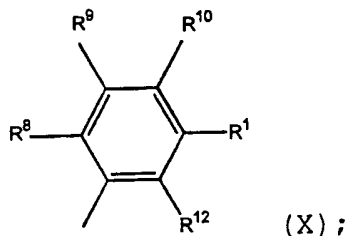
16. The process as recited in claim 15 wherein said compound is (VII).

17. The process as recited in claim 15 wherein said compound is (IX).

5 18. The process as recited in claim 15 wherein said compound is (XII).

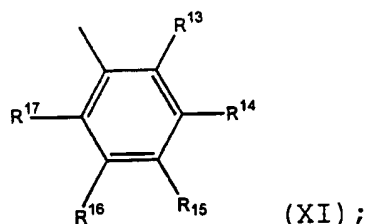
19. The process as recited in claim 15 wherein:

R^6 is



10

R^7 is



R^8 and R^{13} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

15 R^9 , R^{10} , R^{11} , R^{14} , R^{15} and R^{16} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R^{12} and R^{17} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

20 and provided that any two of R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} and R^{17} that are vicinal to one another, taken together may form a ring.

20. The process as recited in claim 15 wherein said temperature is about -50°C to about 100°C .

21. The process as recited in claim 15 wherein M is Fe.

22. The process as recited in claim 15 or 21 wherein R^{21} is n-alkyl.

23. A copolymer of ethylene and a one or more
olefins of the formula $\text{H}_2\text{C}=\text{CHR}^{21}$ wherein said copolymer
has methyl branches and $-\text{R}^{21}$ branches, and wherein the
total of said branches indicate an incorporation of
5 $\text{H}_2\text{C}=\text{CHR}^{21}$ of at least 0.5 mole percent.

24. The copolymer as recited in claim 23 wherein
said incorporation is at least 1 mole percent.

25. The copolymer as recited in claim 23 or 24
wherein each of said methyl branches is attached to a
10 carbon atom, and an $-\text{R}^{21}$ group is also attached to said
carbon atom.

26. The copolymer as recited in claim 23 or 24
wherein R^{21} is n-alkyl.

27. The copolymer as recited in claim 25 wherein
15 R^{21} is n-alkyl.

28. The process as recited in claim 1, 2 or 14
wherein said compound or complex is supported on a
substrate.



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | |
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| (54) Title: COPOLYMERIZATION OF OLEFINS

(57) Abstract

Ethylene and/or propylene, and α -olefins may be copolymerized by contacting them with certain iron or cobalt complexes of selected 2,6-pyridinecarboxaldehydebis(imines) and 2,6-diacetylpyridinebis(imines). The polymers produced, some of which are novel, are useful as molding resins. | | |

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/11549

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/00 C08F210/16 C08F4/26 C08F4/70 C08F4/80

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X | B.L. SMALL, M. BROOKHART AND A.M.A. BENNETT: "Highly Active Iron and Cobalt Catalysts for the Polymerization of Ethylene"
J. AM. CHEM. SOC.,
vol. 120, no. 16,
29 April 1998 (1998-04-29), pages
4049-4050, XP002119954
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the whole document | 1-22 |
| A | EP 0 824 111 A (ATOCHEM ELF SA)
18 February 1998 (1998-02-18)
page 9 | 1-22 |
| P,X | WO 98 27124 A (DU PONT)
25 June 1998 (1998-06-25)
the whole document | 1-22 |
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Van Golde, L

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/11549

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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|------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| P,X | <p>WO 98 30612 A (BROOKHART MAURICE S ;DU
 PONT (US); SMALL BROOKE L (US); UNIV
 NORTH) 16 July 1998 (1998-07-16)
 the whole document</p> <p>-----</p> | 1-22 |

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 99/ 11549

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
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3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
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1 - 22

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

1. Claims: 1-22

A polymerization process comprising contacting at a temperature of -100 AC to 200 AC of (a) a very specific catalyst system with (b) one or both of ethylene and propylene and (c) an alpha-olefin of the formula $H_2C=CHR$, where R is an alkyl group.

2. Claims: 23-28

A copolymer of ethylene and one or more olefins of the formula $H_2C=CHR$, where R is an alkyl group and wherein the copolymer has methylene branches and -R branches.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/11549

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